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Functional, thermal and rheological properties of oat β-glucan modified by acetylation

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ABSTRACT

Fibers of β-glucan have been added to foods for their thickening properties, their ability to form gel at low concentrations, but mainly for their appeal in health promotion. Current analysis evaluates the influence of acetylation (4% and 6% acetic anhydride for 10 and 20 min) on the functional, thermal, morphological and rheological properties of the concentrate containing 31% of oat β-glucan. The degree of substitution of the acetylated β-glucans ranged from 0.03 to 0.12, suitable for use in foods. Acetylation increased the heterogeneity of molecule degradation and promoted a more compacted hole-less microstructure. Functional properties such as the swelling power and bile acid binding capacity were increased by acetylation. The β-glucan gel showed a reduction in hardness and adhesiveness, which was confirmed by its rheological behavior similar to liquid. The above information is relevant to establish the industrial application of acetylated β-glucan.

1. Introduction

Cereal grains, especially barley and oat, contain a non-starch linear polysaccharide, unbranched, and composed of D-glucose linkage by β (1 → 3) and β (1 → 4), known as 'β-glucan'. The presence of β-1 → 3 linkages leads to twists in the chain polymer, allowing water to get in between the chains, and makes β-glucan soluble in water. Therefore, β-glucan, classified as a soluble dietary fiber component (Vasanthan & Temelli, 2008), is a soluble fiber and its intake promotes water absorption and swelling in the gastrointestinal tract, which may be related to lowering the effects of postprandial blood glucose, reduction of serum cholesterol, and insulin responses (Wood, 2007). Further, increases in volume trigger stomach distention, related to the ability of cereal fiber to form a gel-like network, and alter gastrointestinal viscosity (Reimer et al., 2000) which promotes satiety. Since intake of the fiber provides less energy, it may be administrated in weight control and in the prevention and treatment of obesity (Bae, Lee, Kim, & Lee, 2009).

The β-glucan may be used as a thickening agent in food technology since it tends to form viscous solutions and high viscosity gels at low concentrations (Wood, 2004, 2007). The characteristics of β-glucan gels depend on the molecular weight and are modified by chemical, enzymatic, freezing, storage, processing or cooking treatment, and thereby modifying their functional properties (Banchathanakij & Suphantharika, 2009; Wood, 2007).

Research on modifications of β-glucan to change its properties is rare. Studies on the molecular weight reduction of β-glucan have been performed by high pressure homogenization (Kivelä, Pitkänen, Laine, Aseyev, & Sontag-Strohm, 2010), addition of ascorbic acid (Kivelä, Gates, & Sontag-Strohm, 2009), acid or enzymatic depolymerization (Sibakov et al., 2013), and oxidation (Faure, Sánchez-Ferrer, Zabara, Andersen, & Nyström, 2014; Moura et al., 2011).

Chemical modifications by acetylation in β-glucan have not yet been reported in literature, although they have been applied to starch and other polymers. Acetylation is a method of substituting hydroxyl groups in acetyl groups. According to the FDA – Food, Labeling, College Park, and coronary heart disease (2006), the degree of substitution permitted in foods lies between 0.01 and 0.20.

Starch acetylation promotes the introduction of the acetyl group in amylose and amylopectin molecules forming a granular starch ester which has superior properties when compared to its native form. In fact, it has been used to confer higher thermal stability and resistance to retrogradation (Singh, Chawla, & Singh, 2004). According to Colussi et al. (2014), acetylation in rice starch reduces crystallinity, viscosity, swelling power and solubility, and increases thermal stability.

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The objective of this study was to obtain an acetylated β-glucan with an acetylation percentage suitable for use in food, and to evaluate the influence of the degree of acetylation on the functional, thermal, morphological and rheological properties of oat β-glucan.

2. Materials and methods

2.1. Material

Oat bran was supplied by Cerealle Industry and Commerce Ltda Cereals, Pelotas RS Brazil, cultivar IAC-07.

2.2. Extraction and characterization of β-glucan extract

The extraction of β-glucan was conducted by a non-enzymatic method as described by Moura et al. (2011). Oat bran (100 g) was added to distilled water (2.5 L) and submitted to a water bath at 90 °C, under shaking (450 rpm), for 10 min. The mixture was then fragmented in a blender for 5 min, heated again at 90 °C in a heating bath for 50 min under agitation (about 1200 rpm), and centrifuged at 7500 rpm for 20 min. The supernatant to which was added ethyl alcohol 96% 1:1 was kept for 18 h under refrigeration and then dried at 60 °C in an air-circulating oven up to approximately 12% moisture content. After obtaining the required amount, the β-glucan sample was defatted by the Soxhlet method (AOAC, 2005) and triturated in an analytical mill (Model A11, IKA, Werke Staufen, Germany).

2.3. Characterization of β-glucan concentrate

The quantification of β-glucan in the concentrate was performed by an enzymatic method (Approved Method 32-23, AACC, 2000) using the BBG Megazyme kit (Megazyme, Bray, Co. Wicklow, Ireland). Crude fiber, proteins and ash were determined following methods of the American Association of Cereal Chemists (AACC, 2000) and results expressed in d.b. (dry basis). The residual carbohydrates were determined by the difference.

β-Glucan concentrate obtained from oat bran contained 41% crude fiber, 13% protein, 1.5% ash and 44.5% residual carbohydrates. The concentrate contained 31% of β-glucan.

2.4. Acetylation

Acetylation was performed according to Phillips, Huijum, Duohai, and Harold (1999), with modifications. β-Glucan concentrate (25 g) was dispersed in distilled water (1.5 L) and shaken at 2000 rpm, at 24 °C, for 2 h. The suspension's pH was adjusted to 8.0 with aqueous NaOH (3%). Acetic anhydride was slowly added to the slurry at concentrations of 4 and 6% (g acetic anhydride/100 mL β-glucan), adjusting the pH between 8.0 and 8.4 by the alkaline solution. After the complete addition of the acetic anhydride, the reaction was continued for 10 or 20 min and interrupted, setting the pH at 4.5 (0.5 N HCl). The suspension was centrifuged at 7000 rpm for 10 min and subjected to two successive washes with 96% ethanol, under stirring. The sample was dried at 60 °C in an air-circulating oven up to approximately 12% moisture.

2.5. Fourier transform infrared spectroscopy (FT-IR)

Sample preparation and analysis parameters were performed according to Diop, Li, Xie, and Shi (2011). Tablets were prepared from the mixture of the sample with KBr at a ratio of 1:100 (sample: KBr). Infrared spectra of native and modified β-glucan samples were obtained by a Fourier Transform Spectrometer (IR Prestige 21, Shimadzu) in the 4000–400 cm^{-1} region.

2.6. Acetyl percentage, degree of substitution and differential scanning calorimetric (DSC)

The percentage of acetyl groups (Ac%) and degree of substitution (DS) were determined titrimetrically, following the method by Wurzburg (1964).

Thermal properties were evaluated in a differential scanning calorimeter (DSC, TA-60WS, Shimadzu, Kyoto, Japan). The samples (2.5 mg) were weighed in aluminum pans. The pots with samples were heated, together with an empty reference pan under a nitrogen atmosphere 30–200 °C with a 10 °C/min heating ramp.

2.7. Scanning electron microscopy

The microstructure of β-glucan particles was examined by a scanning electron microscope (JEOL, JSM-6610LV, Tokyo, Japan). The samples were dried in absolute ethanol and covered with a thin layer of gold, using a sputter Desk V (New Jersey, USA).

2.8. Swelling power

The swelling power was determined according to methods by Bae et al. (2009), with modifications. A sample of β-glucan (0.3 g) was added to distilled water (10 mL) and placed in a shaking water bath at 70 °C for 10 min, and later transferred to a boiling water bath. After boiling for 10 min, the tubes were cooled with tap water for 5 min and centrifuged at 1700 g for 4 min. Swelling power was expressed as the ratio between wet sediment weight and dry sample weight.

2.9. Fat binding capacity

In vitro fat binding capacity was determined according to the method by Moura et al. (2011), with adaptations. A sample of 0.2 g of β-glucan was added to 10 mL of soy oil, stirred in an Ultraturrax homogenizer (IKA, T18B digital, Werke Staufen, Germany) at 6.500 rpm for 1 min, kept at room temperature for 1 h, with successive agitation every 15 min, and centrifuged at 1600 g for 20 min. The fat binding capacity was determined by the ratio between wet weight and dry weight of a sediment sample.

2.10. Bile acid binding (cholic acid)

The in vitro bile acid binding capacity was measured following Bae et al. (2009), with modifications. Samples were added to a 0.01 M sodium phosphate buffer (pH 7.0) containing 200 mM cholic acid at a concentration of 2.5 mg/mL, stirred at 37 °C for 2 h, and filtered (0.2 mm syringe filter, Waters Co., USA). The resulting solutions (0.2 mL) were treated with 70% sulfuric acid (1 mL) for 5 min and a furfural alcohol solution 0.9% (0.2 mL) was added. Absorbance was measured at 510 nm after 1 h.

2.11. Chemical digestion and glucose availability

The digestive chemical experimental model enables the mimicking, in the laboratory, of in vivo reactions that take place in the stomach and duodenum, as suggested by Rodríguez et al. (2008), with modifications. Glucose availability was performed as below: a mixture of 0.3 g β-glucan, 0.3 g glucose, and 10 mL distilled water was stirred in an Ultraturrax homogenizer (IKA, T18B digital, Werke, Germany), heated to 70 °C for 10 min, and then cooled in tap water. Further, 50 mL of 0.1 M HCl were added so that the pH would be 1.0–2.0 and then taken to the bath at 37 °C for 1 h to reproduce the gastric environment. Formed mixes were taken from an acidic medium to a pH 6.8–7.2 by adding 15 g/L of $NaHCO_3$ which was then maintained at 37 °C for 30 min to reproduce the

duodenal environment. The sham digestion was left to rest for 15 min. Samples were taken from the supernatant to determine glucose. Glucose amounts, determined by the above method, represented the nutrients' bioavailable fraction.

2.12. Gelling properties

The minimum amount of β-glucan concentrate required to form a strong gel was determined by the method described by Moura et al. (2011), with modifications. β-Glucan concentrate dispersions at different levels (3%, 6%, 9% and 12%) were added to 10 mL of distilled water. The dispersions were heated at 90 °C for 1 h, homogenized every 15 min, cooled rapidly, and then refrigerated at 4 °C for 2 h. The tubes were inverted to determine which β-glucan concentrate amounts formed a firm gel; i.e., those that did not fall off or slip down the walls of the tube when inverted.

2.13. Gel texture

The gel texture was determined in a texture analyzer (TA.XT plus, Stable Micro Systems, Godalming, UK). The gel concentration was prepared at 3% in distilled water with an Ultraturrax homogenization (IKA, digital T18B, Werke, Germany) at 4500 rpm, placed in a water bath at 90 °C for 30 min, cooled under tap water, and maintained at 4 °C for 24 h. The gels were compressed to 50% of their height by a cylindrical probe with a 20 mm diameter (P/20) at a speed of 1 mm/s, at room temperature.

2.14. Rheological analyzes

Rheological analyzes were conducted on a rheometer (RS 150, Haake®; Thermo, Waltham MA) using cone and plate geometry (60 mm diameter; 0.104 mm distance, angle of 2° to 25 °C). Viscosity was measured by varying the shear rate from 0.01 to 1000 s^{-1}. The oscillatory measurements were determined by a frequency ranging from 0.1 to 10 Hz in linear viscosity and a strain rate of 0.1%. The suspensions of β-glucan were prepared as described by Bae et al. (2009).

2.15. Statistical analyses

The analyses were performed in triplicate and results were submitted to an analysis of variance ($p \leqslant 0.05$); means were evaluated by Tukey's test ($p \leqslant 0.05$).

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectroscopy confirmed the changes in the chemical structure of β-glucan molecule after acetylation (Fig. 1) when an ester band appeared at 1740 cm^{-1} (C═O), characterizing the incorporation of acetyl groups. A small variation of the intensity of this peak (1740 cm^{-1}) between the acetylated β-glucan was reported, indicating that the degree of substitution was similar. However, it was not possible to measure its intensity by this analysis.

3.2. Acetyl percentage (Ac%) and degree of substitution (DS)

Table 1 shows rates of the percentage of acetyl groups and degree of substitution of the acetylated β-glucans at different levels of acetic anhydride (4% and 6%) and reaction times (10 min and 20 min). An increased level of acetic anhydride and acetylation reaction time increased the percentage of acetyl groups and degree of substitution of acetylated β-glucans (Table 1).

Since no research on acetylated β-glucan is extant, some studies on acetylated starches were used to evaluate the effect of the concentration of acetic anhydride and reaction time, since both molecules were composed of anhydroglucose. The molecule of β-glucan

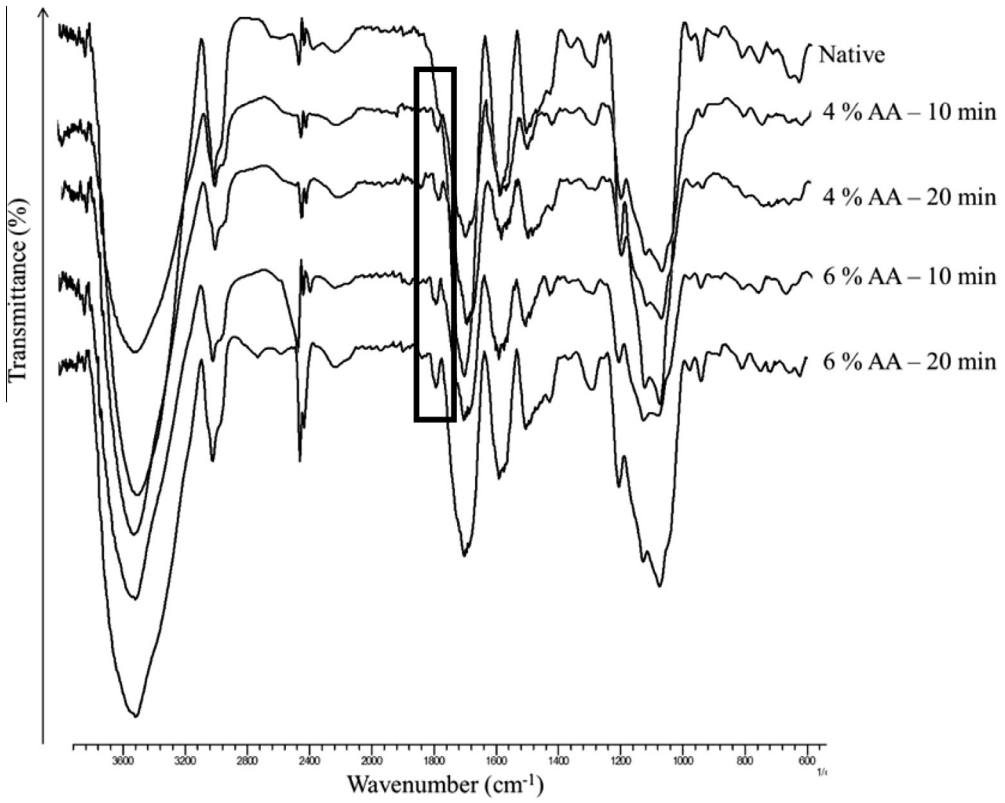

Fig. 1. FT-IR spectroscopy of native and acetylated β-glucans at different concentrations of acetic anhydride and different reaction times.

Table 1
Percentage of acetyl groups (Ac%), degree of substitution (DS) and thermal properties of native and acetylated β-glucans at different concentrations of acetic anhydride and different reaction times.

Treatments[a]	Ac (%)	DS	To (°C)	Tp (°C)	Tc (°C)	Tc – To (°C)	ΔH (J/g)
Native	–	–	160.9	161.2	165.9	5.0	155.1
4% AA – 10 min	0.75 d	0.03 d	154.1	155.2	161.6	7.5	200.9
4% AA – 20 min	1.57 c	0.06 c	155.7	157.0	163.3	7.5	177.8
6% AA – 10 min	2.05 b	0.08 b	159.6	161.0	167.0	7.5	187.7
6% AA – 20 min	2.97 a	0.12 a	155.9	154.5	159.5	3.6	180.5

[a] Different letters in the same column differ statistically ($p < 0.05$).

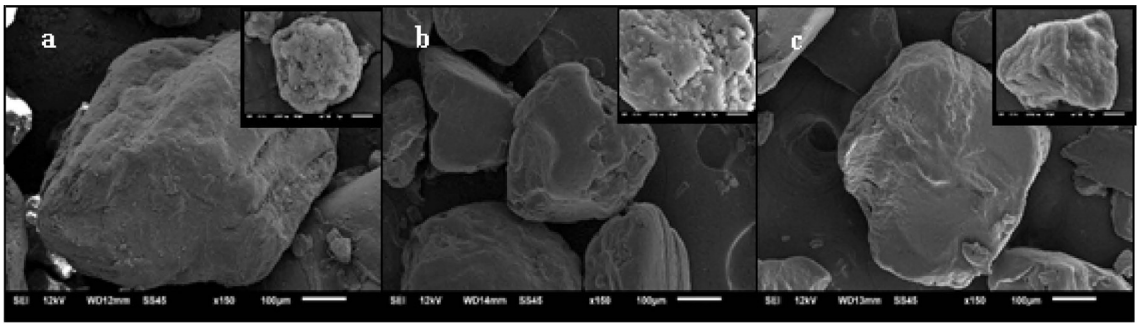

Fig. 2. Scanning electron microscopy for native β-glucan (a); acetylated 4% AA – 10 min β-glucan (b) and acetylated 6% AA – 20 min β-glucan (c).

had a favorable effect on diffusion time and absorption of acetyl groups when compared to starch molecules. This is due to the fact that starch molecules are arranged in the form of granules which hinder access to acetic anhydride, although β-glucan showed similar levels of acetylated starches in the same reaction conditions replacement.

Mbougueng, Tenin, Scher, and Tchiégang (2012) evaluated the effect of acetic anhydride reaction (6%) at different times in potato and cassava starches. Acetyl percentage and DS indicated the difference ($p < 0.05$) in the acetylation reaction time. The DS for cassava starches was 0.10 and 0.26 at 10 min and 20 min of reaction, respectively; in the case of potato starches DS was 0.10 and 0.18.

Mirmoghtadaie, Kadivar, and Shahedi (2009) also reported that an increase from 6% to 8% acetic anhydride in the acetylation of oat starch during 30 min of reaction increased the degree of substitution from 0.05 to 0.11.

The effect of adding different levels of acetic anhydride (2–12%) on acetyl and the degree of substitution of potato and corn starches was studied by Singh et al. (2004). These authors reported that the increase of the substitution degree of acetylated starch was dependent on the acetic anhydride concentration. In the case of potato starch, the DS ranged from 0.18 to 0.24, while corn starch showed a lower DS, ranging from 0.13 to 0.18.

3.3. Differential scanning calorimetric (DSC) measurement

DSC is a useful tool to explain phase transitions and thermal stability technique. The acetylation of β-glucan reduced To and Tp rates and increased degradation enthalpy (ΔH) (Table 1). Between acetylated β-glucan, the treatment of lower DS (4% AA – 10 min) showed a higher reduction in the initial degradation temperature and a higher ΔH increase.

With the exception of β-glucan with a higher DS (6% AA – 20 min), acetylation enlarged the endotherm (Tc–To) when compared to the native β-glucan. Differences in the tracks degradation temperature (Tc–To) of β-glucans suggested that acetylation increased the heterogeneity of molecule degradation, with the exception of the more acetylated β-glucan (Table 1).

Table 2
Swelling power (SP), fat binding capacity (FB), bile acid binding (BAD) and glucose availability (GA) of native and acetylated β-glucans.

Treatments[a]	SP (g/g)	FB (g/g)	BAD (%)	GA (mg/dL)
Native	12.1 e	4.1 a	19.4 b	11.6 c
4% AA – 10 min	14.5 d	2.6 c	20.4 ab	15.1 b
4% AA – 20 min	22.6 a	3.2 b	23.3 a	18.2 a
6% AA – 10 min	15.8 c	2.7 c	21.9 ab	16.8 ab
6% AA – 20 min	18.4 b	3.4 b	19.2 b	19.2 a

[a] Different letters in the same column differ statistically ($p < 0.05$).

3.4. Scanning electron microscopy

Scanning electron microscopy analyzed the changes in the microstructure of β-glucan after acetylation. Fig. 2 demonstrates the micrographs of the native β-glucan, acetylated β-glucan with a lower DS (4% AA and 10 min) and a β-glucan acetylated with higher DS (6% AA – 20 min). The images were displayed at a magnification of 150 times (100 μm range) and amplified for 4000 times (5 μm scale) for a better observation of the particle's surface.

The particles size and shape were not regular. In fact, the acetylated β-glucan had a smoother and more compact surface. When acetylated β-glucan (5 μm scale) was compared with DS increase, the porosity surface of β-glucan decreased, resulting in a fully compacted structure without holes and without the sticking of other particles.

Similar behavior was observed by Luz, Del Tio, Rocha, Gonçalves, and Del'Arco (2008) in cellulose and cellulignin, where native fiber showed a surface with holes while globular and amorphous agglomerates were formed after acetylation.

3.5. Swelling power (SP), fat binding capacity (FB), bile acid binding (BAD) and glucose availability (GA)

The swelling power, fat binding capacities, bile acid binding, and glucose availability of native and acetylated β-glucans are given in Table 2.

The native β-glucan had 12.1 g/g of swelling power, less than that reported by Moura et al. (2011) with 14.5 g/g, and by Bae et al. (2009) with 15.1 g/g. However, both showed higher β-glucan content in the concentrate, respectively 32% and 43% of β-glucan.

Acetylation increased the swelling power of β-glucan. The β-glucan acetylated with 4% AA and 20 min of reaction showed the highest swelling power, with an increase of 87% when compared to the native one (Table 2).

With the elevation of DS over 0.06 (6% AA, 10 and 20 min), there was a decrease in swelling power of b-glucans acetylated, indicating that higher levels of acetylation would trigger breakage of glucoside bonds and reduce the water retention capacity. Bae et al. (2009) also found a reduction in the swelling power in β-glucan when the molecules were partially hydrolyzed with cellulase enzyme, resulting in different molecular weights.

The molecular and structural characteristics of β-glucan are important because they determine their physical properties, such as water solubility and rheological behavior, as well as the functional effects on foods. (Banchathanakij & Suphantharika, 2009). The cellulose segments on the molecular structure of β-glucan may contribute towards the stiffness of the molecules in the solution, due to their insolubility (Varum, Smidsred, & Brant, 1992). β-Glucan containing blocks of adjacent β-(1–4) linkages may exhibit a trend for interchain aggregation, and hence lower solubility due to strong hydrogen bonds along the cellodextrin sections (Lazaridou & Biliaderis, 2007).

Mirmoghtadaie et al. (2009) studied the acetylation of oat starch, also employing the method proposed by Phillips et al. (1999). The swelling power of these polymers, acetylated with 6% and 8%, was higher ($p < 0.05$) than native starch, and increased with rise in acetic anhydride. Sodhi and Singh (2005) studied the acetylation of starches from different varieties of rice by using the same method. They found that acetylation with 6% of acetic anhydride increased swelling power ($p < 0.05$) for all cultivars, which they attributed to the introduction of hydrophilic substituents that retained water molecules to form hydrogen bonds in starch granules.

The hypocholesterolemic effects of cereals containing β-glucan explained by their binding to bile acids, synthesized from cholesterol in the liver and, consequently, its fecal excretion, tend to reduce cholesterol levels in the body (Lazaridou & Biliaderis, 2007).

In a study about the functional benefits of chitosan, Zhou, Xia, Zhang, and Yu (2006) reported that the ability to bind with bile acids and fat is related to the hypocholesterolemic and hypolipidemic effect and affects the lymphatic absorption of cholesterol and fat.

The fat binding capacity of native β-glucan was a 4.1 g oil/g sample. The acetylation of β-glucan resulted in a reduction of fat binding ability. In fact, the acetylated β-glucan with 20 min of reaction showed a higher binding capacity with fat when compared with acetylated β-glucan with 10 min of reaction (Table 2).

Moura et al. (2011) chemically modified β-glucan by oxidative treatment and reported that this modification did not affect the binding with the fat, whereas the native β-glucan showed 4.1 g of oil/g sample. The in vitro study of fat binding capacity for β-glucan hydrolyzed enzymatically, conducted by Bae et al. (2009), demonstrated that samples with lower molecular weight generally exhibited a higher fat binding capacity than native β-glucan, with 3.9 g oil/g sample.

Native β-glucan had 19.4% bile acids binding capacity, showing that acetylation of the molecule had a positive impact on this property. The acetylated β-glucan with 4% AA and 20 min of reaction showed the highest bile acids binding capacity (Table 2).

Moura et al. (2011) reported that bile acids binding ability in native β-glucan was 11.3% and increased with oxidative treatment. Bae et al. (2009) reported that native β-glucan (not enzymatically hydrolyzed) presented bile acid binding capacity of 13.1%. Although these authors did not find a linear correlation of this property with an increasing degree of hydrolysis, the β-glucans with a lower molecular weight showed the highest bile acids' binding ability (26.5%).

Andersson, Ellegård, and Andersson (2002) observed that consumption of β-glucan doubles the serum concentration of 7α-hydroxy-4-cholesten-3-one (α-HC), the metabolite that causes the regulation of bile acids synthesis, synthesized from cholesterol in the liver. The increased production/excretion of bile acids stimulates the absorption of cholesterol in the liver, which reduces the concentration of serum cholesterol.

The bioavailable fraction of glucose in native β-glucan was 11.6%. Acetylation increased the availability of this nutrient and reached maximum levels when the DS was higher than 0.06, lowering the hypoglycemic effects from the fiber.

In a research that compared the effects of various dietary fibers in the bioavailability of glucose, Rodríguez et al. (2008) found that dietary fibers, such as psyllium and chitosan, exhibited the greatest reductions in glucose viability, 17.7 and 15.3%, respectively, when compared with apple fiber, wheat fiber, bamboo fiber and inulin. These authors highlighted that their study foregrounded the idea that dietary fibers, with the exception of apple fiber, reduced the absorption rate of glucose, of which the most effective was chitosan. The behavior for delay absorption probably altered the response of the endocrine system by transporting material in the lower part of the small intestine before absorption and by the production of a more constant blood glucose profile.

3.6. Gelling properties and gel texture

The gelling properties of β-glucan determined the minimum amount of β-glucan concentrate which was necessary to form a strong gel (i.e., that does not fall off the sides in inverted test tubes), or rather, 3%. The amount of water was insufficient to solubilize the β-glucan concentrate in any other percentage (6%, 9% and 12%). Consequently, the concentration of 3% of β-glucan was appropriate for gel texture tests.

Hardness, adhesiveness, cohesiveness, elasticity and tackiness were investigated in gels of native and acetylated β-glucans, shown in Table 3. Hardness is defined as the force required to cause any deformity (Bourne, 2002). Acetylated β-glucan gel with DS 0.03 showed a similar hardness to that presented by native β-glucan. In the treatment with 4% acetic anhydride and 20 min of reaction,

Table 3
Texture profile of native and acetylated β-glucan gels.

Treatments[a]	Hardness (N)	Adhesiveness (g s^{-1})	Cohesiveness	Springiness (mm)	Gumminess (N)
Native	0.169 a	−0.802 a	0.919 b	1.025 d	0.151 b
4% AA – 10 min	0.158 ab	–	1.038 b	1.778 c	0.153 b
4% AA – 20 min	0.132 b	–	2.758 a	1.209 cd	0.193 b
6% AA – 10 min	0.136 b	–	3.236 a	13.692 a	0.453 a
6% AA – 20 min	0.101 c	–	3.193 a	12.152 b	0.395 a

[a] Different letters in the same column differ statistically ($p < 0.05$).

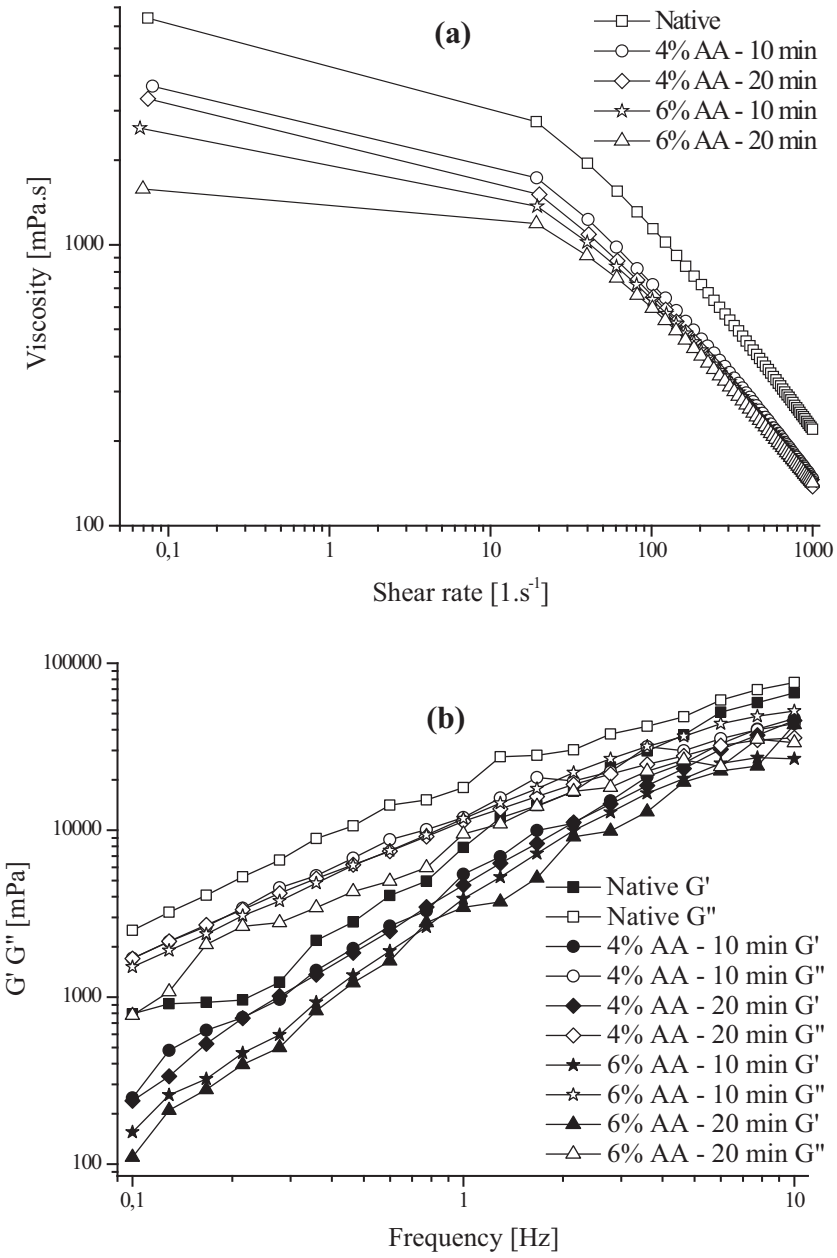

Fig. 3. Viscosity of gels 3% of native and acetylated β-glucan (a); linear viscoelastic measurements of dynamic frequency oscillation of gel 3% of native and acetylated β-glucans (b).

a decrease in hardness occurred due to the addition of acetyl groups in the molecule of β-glucan (Table 3).

Adhesiveness indicates the force required to remove the probe from the gel after compression, or rather, a combination of adhesive and cohesive strength (Huang, Kennedy, Li, Xu, & Xie, 2007). Acetylated β-glucan did not show any adhesiveness (Table 3). Cohesiveness measures the degree of difficulty in breaking down the gel's internal structure (Bourne, 2002). The β-glucan gel with a higher DS showed a higher cohesiveness when compared to native and acetylated β-glucan gel with a slower DS (4% AA – 10 min). Springiness is the rate at which a deformed material returns to its initial condition after the force is removed (Bourne, 2002). The springiness was significantly ($p < 0.05$) affected by acetylation and was higher when the acetic anhydride level increased from 4% to 6%. Gumminess is the necessary force to disintegrate the material (Bourne, 2002). The gumminess was also strongly affected by acetylation. The β-glucan gels from acetylated DS 0.08 (6% AA – 10 min) showed an increase in gumminess when compared to native β-glucan gel.

The reduction in hardness and lack of adhesiveness of acetylated β-glucan gels, combined with increased cohesiveness, springiness and gumminess, are characteristics which improve the use of β-glucan in the case of pumping on the industrial scale, or the fiber's dispersion and solubilization in food applications.

3.7. Rheological analyses

β-Glucan is a linear polysaccharide with high molecular weight and has a high volume occupancy in solutions (high intrinsic viscosity). High volume occupancy leads to polymer coil overlap and entanglement at low concentrations (0.2–0.3% w/v). Viscosity is enhanced due to concentration and molecular weight (Ren,

Ellis, Ross-Murphy, Wang, & Wood, 2003). Fig. 3a shows viscosity curves of native and acetylated β-glucan, with an increasing shear rate. Viscosity of the gels was reduced and confirmed the pseudoplastic behavior of gels, similar to that reported by Zhao et al. (2014) on oat, wheat and barley β-glucans.

Ren et al. (2003) reported a higher viscosity of β-glucan dispersions of 2.7% when compared to our study. However, the β-glucan concentrate in the above assay was composed of 80% β-glucan, superior to the concentrate studied in current analysis (31% of β-glucan). Lee and Inglett (2006), using a 2.5% dispersion containing 15.6% β-glucan from barley, registered a lower viscosity when compared to β-glycan in current study.

Native β-glucan was more viscous than acetylated β-glucan, probably due to a lower swelling power, characterized by the smallest amount of water retained between molecules. The acetylated β-glucan, at a low shear rate viscosity, was apparently different between treatments; viscoelastic behavior was similar with an increasing shear rate. The reduction in viscosity due to acetylation favors the application of β-glucan at industrial level by a higher flow capacity and dispersion.

Fig. 3b shows linear viscoelastic property from dynamic frequency oscillation measurements of native gel 3% and acetylated β-glucan. In all measures of frequency G" was higher than G', indicating that β-glucan had a viscous behavior similar to a liquid under the conditions studied.

Xu, Inglett, Chen, and Liu (2013) evaluated different dispersions of β-glucan and found that in a 10% solution, which contained 30% β-glucan, at frequencies up to 2 Hz, the viscous modulus were higher than the elastic modulus; there was a reversal of modules above this frequency. However, Zhao et al. (2014) found similar behavior to that in a current study for native β-glucan, using a 5% solution containing 75.9% of β-glucan in the concentrate. Current results and those reported in the literature show that the relationship between the rheological properties and the concentration of β-glucan in solution are still not fully understood.

The elastic (G′) and viscous (G″) modulus of β-glucan increased with rising frequency. The β-glucan with more intense acetylation, whose DS was 0.08 and 0.12, had the lowest G′ and G″ rates. In addition, there was a crossover of G′ and G″ at high frequencies for acetylated β-glucan with 4% and 6% of acetic anhydride and 20 min of reaction, characterizing the process of acetylation with a higher degree of substitution, which may possibly impart gel-like properties. Module crossing was also observed by Xu et al. (2013) in samples of native β-glucan, albeit in a 10% dispersion. Lee and Inglett (2006) also registered the behavior of β-glucan solutions in low concentrations (2.5% dispersion), or rather, G" was higher than G′, confirming results obtained in the current assay. However, at higher concentrations (dispersions of 5 and 7.5%) G′ was superior to G″.

4. Conclusion

The acetylation of β-glucan promoted the incorporation of acetyl groups in the molecule, resulting in a degree of substitution between 0.03 and 0.12, allowing food application. Acetylation of the β-glucan molecule increased the availability of glucose and reduced the fat binding capacity, reducing fiber functionality. However, increased swelling power and the bile acids' binding capacity increased, which were equally important functional properties. The acetylated β-glucan gel decreased in hardness and did not show adhesiveness when compared to native β-glucan gel. Further, it showed an increase in cohesiveness, springiness and gumminess. Increased levels of acetylation on β-glucan reduced viscosity and showed viscous behavior similar to the liquid. Thus, the acetylation of β-glucan promotes the gels' formation with a functional appeal and better features for industrial applications in food production.

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References

American Association of Cereal Chemists. (2000). Approved methods of the AACC, 10th ed. Methods 32-23, 46-13, 08-01. The Association: St. Paul, MN.

Andersson, M., Ellegård, L., & Andersson, H. (2002). Oat bran stimulates bile acid synthesis within 8 h as measured by 7 alpha-hydroxy-4-cholesten-3-ones. *American Journal of Clinical Nutrition, 76*, 1111–1116.

Bae, I. Y., Lee, S., Kim, S. M., & Lee, H. G. (2009). Effect of partially hydrolysed oat β-glucan on the weight gain and lipid profile of mice. *Food Hydrocolloids, 23*, 2016–2021.

Banchathanakij, R., & Suphantharika, M. (2009). Effect of different β-glucans on the gelatinisation and retrogradation of rice starch. *Food Chemistry, 114*, 5–14.

Bourne, M. C. (2002). Principles of objective texture measurement. In S. L. Taylor (Ed.), *Food texture and viscosity: Concept and measurement* (pp. 182–186). San Diego: Academic Press.

Colussi, R., Pinto, V. Z., Halal, S. L. M., Vanier, N. L., Villanova, F. A., Silva, R. M., et al. (2014). Structural, morphological, and physicochemical properties of acetylated high-, medium-, and low-amylose rice starches. *Carbohydrate Polymers, 103*, 405–413.

Diop, C., Li, H. L., Xie, B. J., & Shi, J. (2011). Effects of acetic acid/acetic anhydride ratios on the properties of corn starch acetates. *Food Chemistry, 126*, 1662–1669.

Faure, A. M., Sánchez-Ferrer, A., Zabara, A., Andersen, M. L., & Nyström, L. (2014). Modulating the structural properties of β-D-glucan degradation products by alternative reaction pathways. *Carbohydrate Polymers, 99*, 679–686.

FDA – Food and Drug Administration. Office of Nutritional Products, Labeling and Dietary Supplements (hfs-800). 5100 Paint Branch Parkway, College Park, MD 20740. Petition for health claim: Barley beta fiber and coronary heart disease, January 27, 2006.

Huang, M., Kennedy, J. F., Li, B., Xu, X., & Xie, B. J. (2007). Characters of rice starch gel modified by gellan, carrageenan, and glucomannan: A texture profile analysis study. *Carbohydrate Polymers, 69*, 411–418.

Kivelä, R., Gates, F., & Sontag-Strohm, T. (2009). Degradation of cereal β-glucan by ascorbic acid induced oxygen radicals. *Journal of Cereal Science, 49*, 1–3.

Kivelä, R., Pitkänen, L., Laine, P., Aseyev, V., & Sontag-Strohm, T. (2010). Influence of homogenisation on the solution properties of oat β-glucan. *Food Hydrocolloids, 24*, 611–618.

Lazaridou, A., & Biliaderis, C. G. (2007). Molecular aspects of cereal β-glucan functionality: Physical properties, technological applications and physiological effects. *Journal of Cereal Science, 46*, 101–118.

Lee, S., & Inglett, G. E. (2006). Functional characterization of steam jet-cooked β-glucan-rich barley flour as an oil barrier in frying batters. *Food Engineering and Physical Properties, 71*, 308–313.

Luz, S. M., Del Tio, J., Rocha, G. J. M., Gonçalves, A. R., & Del'Arco, A. P. Jr., (2008). Cellulose and cellulignin from sugarcane bagasse reinforced polypropylene composites: Effect of acetylation on mechanical and thermal properties. *Composites: Part A, 39*, 1362–1369.

Mirmoghtadaie, L., Kadivar, M., & Shahedi, M. (2009). Effects of cross-linking and acetylation on oat starch properties. *Food Chemistry, 116*, 709–713.

Mbougueng, P. D., Tenin, D., Scher, J., & Tchiégang, C. (2012). Influence of acetylation on physicochemical, functional and thermal properties of potato and cassava starches. *Journal of Food Engineering, 108*, 320–326.

Moura, F. A., Pereira, J. M., Silva, D. O., Zavareze, E. R., Moreira, A. S., Helbig, E., et al. (2011). Effects of oxidative treatment on the physicochemical, rheological and functional properties of oat β-glucan. *Food Chemistry, 128*, 982–987.

Official methods of analysis of AOAC International (2005) 18th ed. Gaithersburg, MD, USA.

Phillips, D. L., Huijum, L., Duohai, P., & Harold, C. (1999). General application of Raman spectroscopy for the determination of level of acetylation in modified starches. *Cereal Chemistry, 76*, 439–443.

Ren, Y., Ellis, P. R., Ross-Murphy, S. B., Wang, Q., & Wood, P. J. (2003). Dilute and semi-dilute solution properties of (1 → 3), (1 → 4)-β-D-glucan, the endosperm cell wall polysaccharide of oats (*Avena sativa* L.). *Carbohydrate Polymers, 53*, 401–408.

Reimer, A. R., Thomson, A. B. R., Rajotte, R. V., Basu, T. K., Ooraikul, B., & McBurney, M. I. (2000). Proglucagon messenger ribonucleic acid and intestinal glucose uptake are modulated by fermentable fibre and food intake in diabetic rats. *Nutrition Research, 20*, 851–864.

Rodríguez, M. S., Montero, M., Staffolo, M. D., Staffolo, M., Bevilacqua, A., & Albertengo, L. (2008). Chitosan influence on glucose and calcium availability from yogurt: In vitro comparative study with plants fibre. *Carbohydrate Polymers, 74*, 797–801.

Sibakov, J., Myllymäki, O., Suortti, T., Kaukovirta-Norja, A., Lehtinen, P., & Poutanen, K. (2013). Comparison of acid and enzymatic hydrolyses of oat bran β-glucan at low water content. *Food Research International, 52*, 99–108.

Singh, N., Chawla, D., & Singh, J. (2004). Influence of acetic anhydride on physico-chemical, morphological and thermal properties of corn and potato starch. *Food Chemistry, 86*, 601–608.

Sodhi, N. S., & Singh, N. (2005). Characteristics of acetylated starches prepared using starches from different rice cultivars. *Journal of Food Engineering, 70*, 117–127.

Varum, K. M., Smidsred, O., & Brant, D. A. (1992). Light scattering reveals micelle-like aggregation in the (1 → 3), (1 → 4) – β-D-glucans from oat aleurone. *Food Hydrocolloids, 5*, 497–511.

Vasanthan, T., & Temelli, F. (2008). Grain fractionation technologies for cereal beta-glucan concentration. *Food Research international, 41*, 876–881.

Wood, P. J. (2004). Relationships between solutions properties of cereal β-glucans and physiological effects – A review. *Trends in Food Science and Technology, 15*, 313–320.

Wood, P. J. (2007). Cereal β-glucans in diet and health. *Journal of Cereal Science, 46*, 230–238.

Wurzburg, O. B. (1964). Acetylation. In R. L. Whistler (Ed.), *Methods in carbohydrate chemistry* (pp. 240). Boca Ratón, FL: Academic Press.

Xu, J., Inglett, G. E., Chen, D., & Liu, S. X. (2013). Viscoelastic properties of oat β-glucan-rich aqueous dispersions. *Food Chemistry, 138*, 186–191.

Zhao, Q., Hu, X., Guo, Q., Cui, S. W., Xian, Y., You, S., et al. (2014). Physicochemical properties and regulatory effects on db/db diabetic mice of β-glucans extracted from oat, wheat and barley. *Food Hydrocolloids, 37*, 60–68.

Zhou, K., Xia, W., Zhang, C., & Yu, L. (2006). In vitro binding of bile acids and triglycerides by selected chitosan preparations and their physico-chemical properties. *LWT – Food Science and Technology, 39*, 1087–1092.